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Thermal decomposition of calcium hydroxide deposited on the substrate

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Abstract

Calcium hydroxide particles deposited on substrates have been investigated by thermal analysis. Dehydration was successfully detected by DSC (heating rate, 1–20°C min^{-1}) for the specimen (thickness about 0.80–2.57 μm) as-deposited on the glass substrate (5 mm × 5 mm × 0.15 mm). The peak temperature and the heat of dehydration ($278 \pm 10\ \mathrm{cal\ g}^{-1}$) was independent of the thickness in the present study. The deviation from the thermochemical data ($328\ \mathrm{cal\ g}^{-1}$) was explained semi-quantitatively as being due to $CaCO_3$ impurity; this hypothesis was supported by the TG–DTA of the deposit removed from the bottom of the vessel.

INTRODUCTION

It is known experimentally or presumptively that solid state reaction is strongly influenced by topochemical factors such as the size and configuration of powder specimens and specimen containers, packing density of powders in the container, ventilation of gases evolved from the specimen, etc. A recent study by Lee et al. [1] showed that thermal decomposition of calcium hydroxide in vacuo occurred at a lower temperature than in a nitrogen flow under atmospheric pressure. Morita et al. [2] proposed preparing a substrate, for what they called "hydrogen bond epitaxy", by topotactic decomposition of calcium hydroxide thin films deposited epitaxially on a magnesium oxide single crystal. The thermal changes of thin films are expected to be different from those of the bulk materials. The present authors reported [3] that thermal oxidation of indium(III) 2-ethylhexanoate film occurred at a notably lower temperature than that of the bulk. This result showed that thermal analysis of thin films is necessary and possible [4–6] although some difficulties must be overcome.

In the present paper, the thermal decomposition process of calcium

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hydroxide films with flat surfaces, but having particles dispersed on the substrates is studied. The system can be approximated to thin films so that this work can be a feasibility study for thermal analysis of hydroxide films.

EXPERIMENTAL

An aqueous solution of calcium hydroxide (0.10 g/100 ml; reported solubility 0.185 g/100 ml at 0°C and 0.077 g/100 ml at 100°C [7]) was kept at about 25°C for 1 day before filtration. The powder remaining on the filter consisted of $CaCO_3$; the endothermic mass loss (42.1%) at about 730°C (heating rate, 10°C min^{-1}) agreed with the expected value (44.0%). The solution was then evaporated in a nitrogen atmosphere at about 60°C to obtain the deposit on the glass substrates (Matsunami Co. Ltd., micro coverglass, 5 mm × 5 mm × 0.15 mm) placed on the bottom of the vessel. The volume of the solution in the vessel was controlled to obtain various amounts of deposit per unit area.

The substrate with a deposit on its upper surface was placed on the specimen holder of the DSC apparatus (Rigaku 8240D, heat flux type) and a substrate without a deposit was used as reference material. The apparatus was calibrated with indium, tin and lead placed on the glass substrate. An ultramicrobalance (Sartorius S4) was used to weigh the substrate with and without the deposit before and after thermal analysis. Since the maximum temperature for the DSC was limited to 500°C, TG–DTA (Rigaku 8101D, twin holder type) was used with platinum containers and Al_2O_3 reference material; the deposit on the bottom surface of the vessel was removed with a spatula.

All the thermal analyses were performed in air. The heating rate was 10°C min^{-1} unless otherwise stated. A Rigaku TAS-300 system (HP Apollo 9000/425e) was used for system control and data processing. The specimens as-deposited on the larger and thicker glass substrate were investigated with an X-ray diffractometer (Rigaku RAD III C) with nickel-filtered copper radiation; 45 kV, 40 mA. A scanning electron microscope (JEOL JAMP-7100) was used for gold coated specimens with an acceleration voltage of 20 kV.

RESULTS AND DISCUSSION

Characterization of the specimen

The SEM photographs for the deposits are shown in Fig. 1. Hexagonal platelets and prisms disposed on the substrate were attributed to the main composition (probably single or twin crystals of $Ca(OH)_2$); crystal growth along the *c* axis was expected. The SEM photographs with higher magnification are shown in Fig. 2. Small grains on the unheated surface (Fig. 2A) disappeared upon heating (Fig. 2B). Although no flat film was

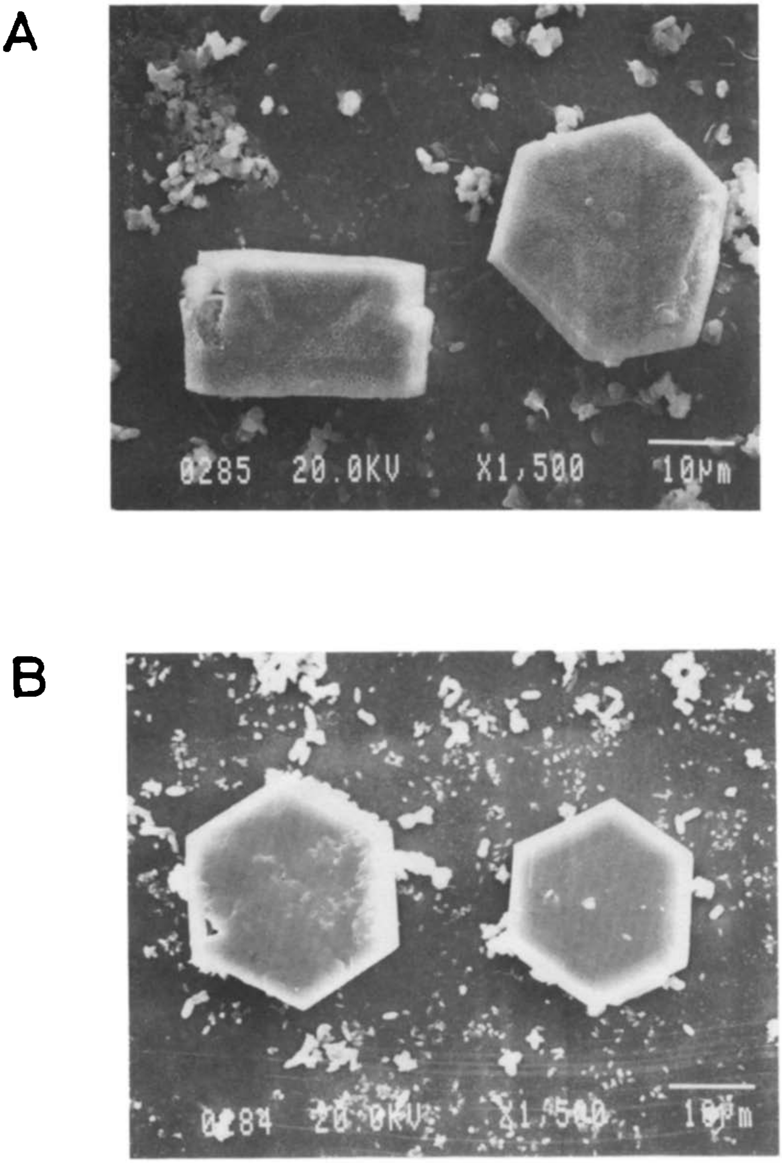

Fig. 1. Scanning electron micrographs for the deposits with reduced film thicknesses of 1.04 µm (A and B) and 3.07 µm (C and D). A and C, unheated; B and D, after thermal analysis (10°C min^{-1} to 500°C in air).

observed, for convenience a reduced film thickness was tentatively estimated for the deposit in the present paper by assuming the deposit to be a uniform film of $Ca(OH)_2$.

The X-ray diffraction spectrum for a typical deposit is shown in Fig. 3. The deposit consisted of $Ca(OH)_2$ [8]; (001) preferred orientation was observed. Weak peaks assigned to $CaCO_3$ [9] impurity were detected only

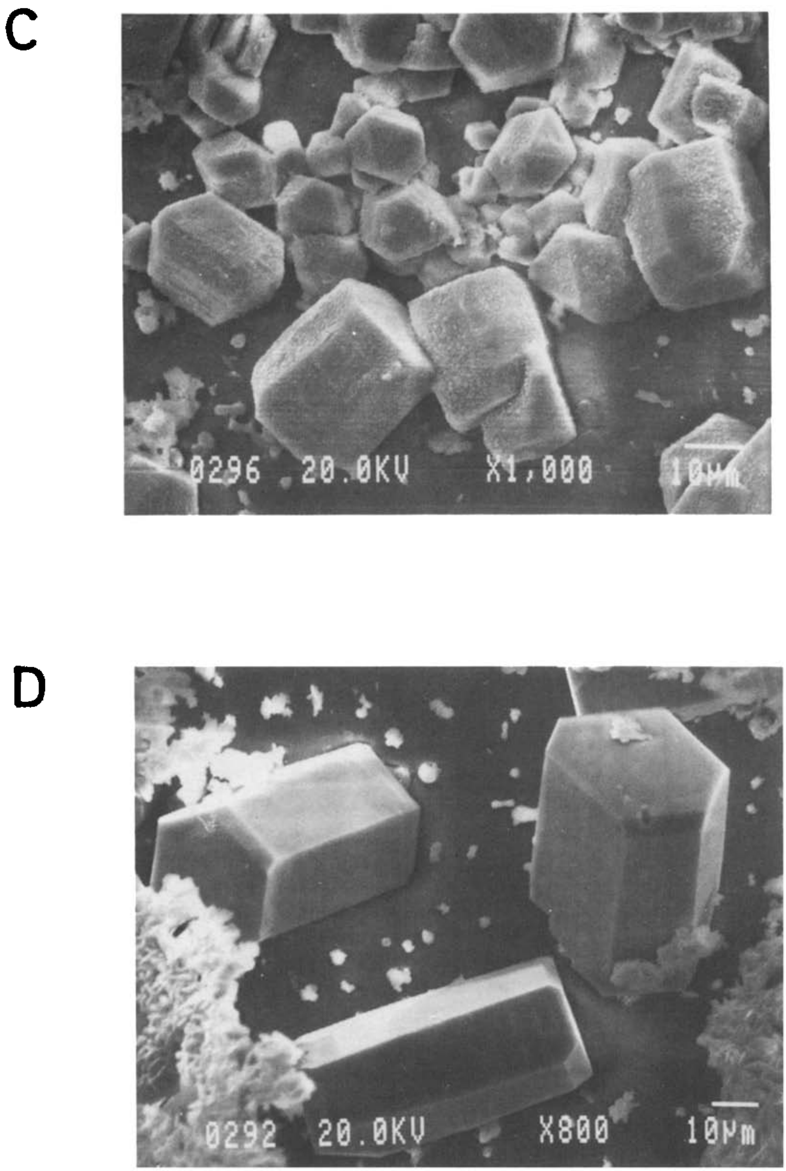

Fig. 1—(continued)

for thick deposits. The small amounts of $CaCO_3$ could not be distinguished from the SEM photographs; they were expected to exist as very small particles on the surface of the $Ca(OH)_2$ crystals and/or the surface of the substrate.

DSC for the specimen as-deposited on the substrate

The DSC results for the deposits on the substrate are shown in Fig. 4. The endothermic peak assigned to the dehydration was successfully

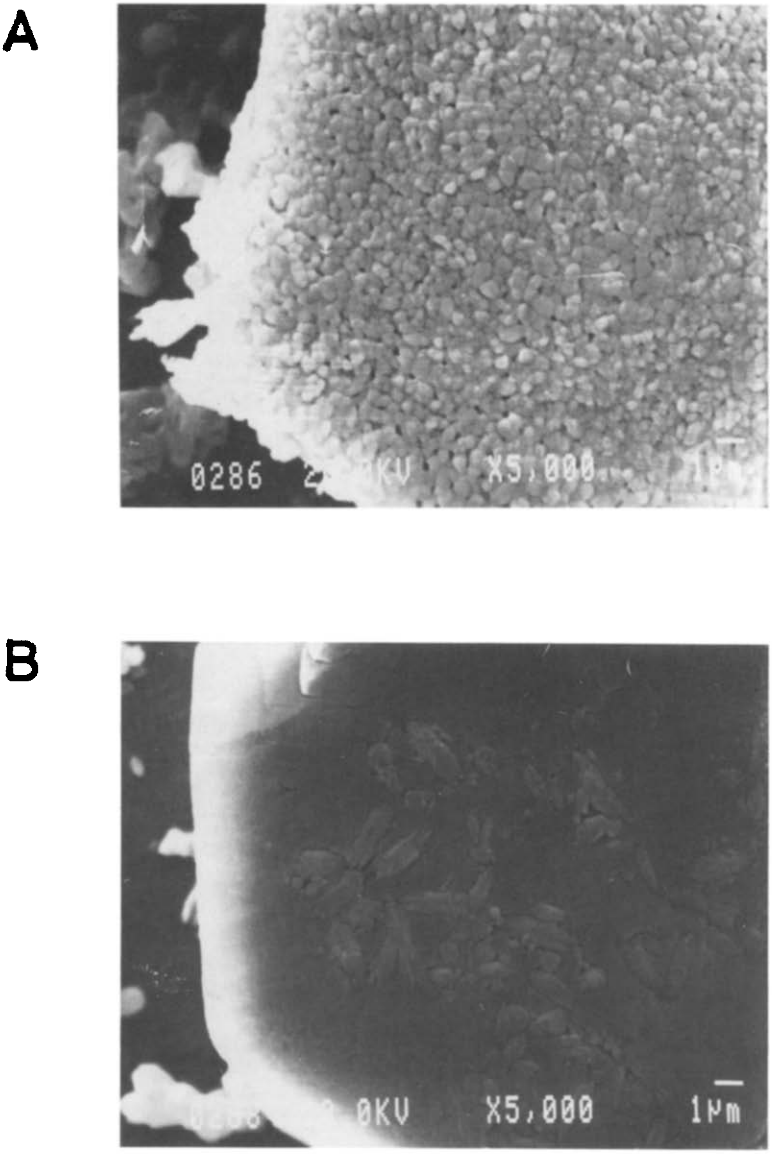

Fig. 2. Scanning electron micrographs for the deposits at higher magnification with reduced film thickness of 1.04 μm. A, unheated; B, after thermal analysis (10°C min^{-1} to 500°C in air).

detected clearly even for the thinner deposit (reduced thickness, 0.80 μm) at the slowest heating rate (1°C min^{-1}) as shown in Fig. 4D. The dependence of the peak temperature on the heating rate is shown in Fig. 5. The peak temperature increased when the sample was heated rapidly. No systematic correlation between the peak temperature and the reduced film

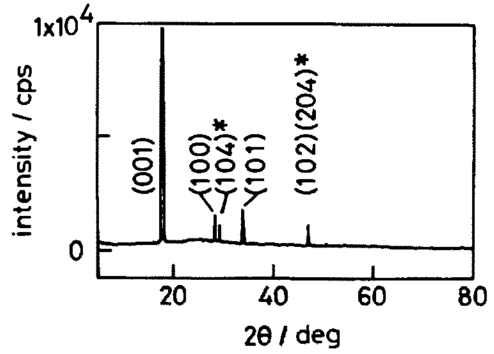

Fig. 3. X-ray diffraction spectrum for a typical deposit with reduced film thickness of 2.57 μm. Values in parentheses are the indexes of diffraction for $CaCO_3$ (with asterisk) and $Ca(OH)_2$ (without asterisk).

thickness was observed under the present experimental conditions, probably because the reaction boundary is parallel to the *c*-axis of the crystal, as reported by Gordon and Kingery [10] for the analogous compound $Mg(OH)_2$. The endothermic heat was independent of the reduced film thickness (0.80–2.57 μm). The data (278 ± 10 cal g^{-1}) corres-

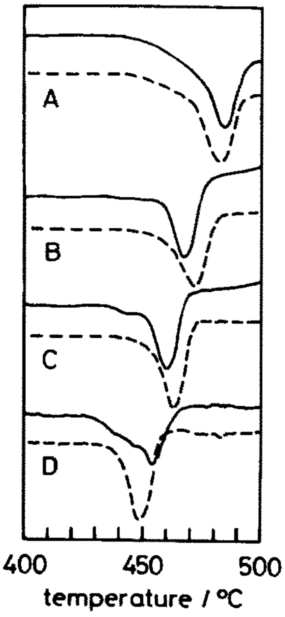

Fig. 4. DSC for the deposits on the substrate with heating rates of 20°C min^{-1} (curve A), 10°C min^{-1} (curve B), 3°C min^{-1} (curve C) and 1°C min^{-1} (curve D). The ordinate is normalized with respect to specimen mass and heating rate. Reduced film thickness are 0.80 μm (solid line) and 1.96 μm (broken line).

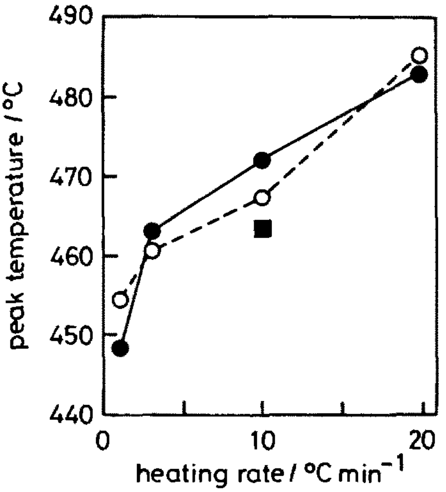

Fig. 5. Dependence of the peak temperature on the heating rate. Reduced film thicknesses are 0.80 μm (solid line) and 1.96 μm (dotted line); ■ is the peak temperature of the TG–DTA in Fig. 6 for the deposit on the bottom of the vessel.

ponded to 85 ± 3% of the heat of dehydration calculated from the thermochemical data (328 cal g^{-1}) [11].

TG–DTA for the specimen removed from the bottom of the vessel

The results of TG–DTA for the deposit removed from the bottom of the vessel are shown in Fig. 6 in order to make a comparision with those deposited on the substrate. A small mass loss (1.2%) at about 300°C may be attributed to dehydration of extremely fine particles of $Ca(OH)_2$; the corresponding endothermic phenomenon should be under the detection limit.

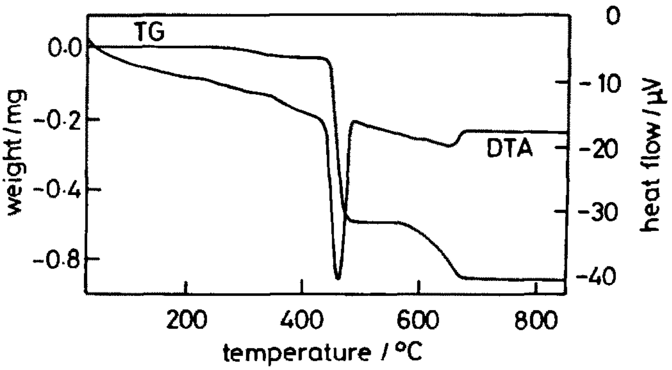

Fig. 6. TG–DTA for the deposit removed from the bottom of the vessel with reduced film thickness of 2.57 μm and specimen mass 2.582 mg.

A drastic mass loss (18.4%) with an endothermic peak at about 460°C should be assigned to the decomposition of $Ca(OH)_2$. This peak temperature is plotted in Fig. 5; the difference is negligible compared with the influence of the heating rate. Another mass loss (6.4%) with an endothermic peak at about 650°C was assigned to the decomposition of $CaCO_3$; in all probability $CaCO_3$ could not be completely eliminated from the deposit. The basic calcium carbonate $2CaCO_3 \cdot Ca(OH)_2 \cdot 1.5H_2O$ reported by Tanaka et al. [12] should be neglected since it is expected to form $CaCO_3$ and $Ca(OH)_2$ under the present experimental conditions. The molar ratio $CaCO_3/(Ca(OH)_2 + CaCO_3)$ estimated from the mass loss was about 12%. Considering this $CaCO_3$ content, the heat of dehydration is estimated to be about 84% of that of pure $Ca(OH)_2$. The deviation (about -16%) agreed with the value obtained by DSC ($-15 \pm 3\%$). This result shows it is possible that the carbonate concentration can be determined quantitatively for film-like specimens if the measurement is sufficiently accurate.

CONCLUSIONS

Thermal decomposition was successfully detected by DSC for calcium hydroxide particles as-deposited on a glass substrate. The deviation between the detected heat of dehydration and that expected from thermochemical data was explained by the presence of $CaCO_3$ impurity.

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